TARNISHING OF DENTAL GOLD ALLOYS

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SUMMARY

This study was initiated to elucidate the reactions occurring during the formation of tarnish on dental gold alloys. The tarnishing of dental gold alloys with and without palladium in sodium sulfide solution was investigated by electrochemical methods and microanalysis of the surface films formed during exposure.

The results showed that Cu_2O, CuS, Cu_2S, and Ag_2S were the reactions which could occur on the surface of the gold alloys in the simulated oral environment. Ag_2S was identified by Auger analysis as being the major constituent present in the tarnish film. Polarization curves in deaerated buffer solutions verified the possible formation of Cu_2O on the surface of these alloys. From the polarization curves, CuS and Cu_2S were also observed as possible compounds which could form in a simulated oral environment, but these were not identified in analysis of the tarnish films. The addition of palladium to gold alloys decreases the susceptibility of the alloys to tarnishing. It is suggested that the palladium addition increases the activation energy for the reaction of silver with sulfur. This may be the result of increased bonding strength between palladium and silver atoms in the alloy. All of the gold alloys showed casting porosity which seemed to increase the susceptibility to tarnishing.

CHAPTER I

INTRODUCTION

The prevention of corrosion and tarnish of metallic restorations in the mouth is of considerable importance and worthy of the time and effort spent on its study. There have been basically two types of approaches to the problem: (1) the development of inert coating materials, and (2) the development of new metallic alloys which are less susceptible to such reactions. Surface coating materials have generally found little application to dental restorations. As a result, the more promising approach has been the development of new alloys which are able to resist the effects of the oral environment.

Tarnish will be defined as a surface discoloration of a metal induced by a chemical or electrochemical reaction between the metal and oral environment. The tarnish may arise from the formation of thin films such as oxides, sulfides, and chlorides. The discoloration associated with tarnish has also been attributed to pigment producing bacteria, absorbed food debris, and drugs containing metals such as iron and mercury.

Sulfur is probably one of the most important elements to be considered with respect to tarnish of metallic restorations. Sulfur is present in many foods and drugs, e.g., eggs, any type of high protein food, and medical sulfide drugs. Thus, the sulfur content of ingested foods can provide the sulfur concentration which is needed for tarnishing of metallic restorations in the oral environment.

Sulfide tarnish has been observed and identified on metallic

restorations in the mouth. X-ray diffraction patterns of clinically tarnished amalgam restorations indicate complex sulfides to be the dominant factor in discoloration with only trace amounts of chloride and other compounds present (1). Clinically tarnished gold alloys were analyzed with an electron probe and the film was found to be composed essentially of a sulfide intermixed with a carbonaceous material. It was noted that in both types of restorations the presence of areas of porosity favored the formation of tarnish (2).

Sulfide vapors were used at one time to test the susceptibility of gold alloys to tarnish (3). Gold alloys containing at least 65 per cent precious metal were noted as being tarnish resistant in the presence of sulfide vapors. Swartz, Phillips, and El Tanner (4) observed that low carat gold alloys (gold less than 75 per cent by weight) would tarnish in a solution of 0.5 per cent sodium sulfide (Na_2S). The high carat gold alloys (75 per cent of gold by weight) showed no observable tarnish in the sodium sulfide solution.

The variables involved in the tarnish of dental gold alloys in 5 per cent sodium sulfide were studied by Von Mohr (5). The tarnish appeared as spotty discolorations over the entire surface of the gold alloy. Von Mohr noted that the areas of porosity showed the first signs of tarnish. This porosity is inherent in all cast gold alloys as the result of solidification shrinkage and entrapped gases. The porosity generally appears as localized shrinkage, microporosity, pinhole porosity, or subsurface porosity (6). Those forms of porosity observed in most cast gold alloys are usually a combination of two or more of the above types.

Tuccillo and Nielsen (2) examined the appearance of tarnish when

gold alloys were immersed in a 0.5 per cent sodium sulfide solution. They noted that the tarnish appeared as uniformly distributed speckled dots covering the surface of the gold alloy. They further postulated that silver was the principal element which rendered the gold alloys susceptible to tarnish and mentioned that surface variations resulting in local anodic-cathodic relationships may exist giving rise to the discontinuous attack appearing on the surface of the metal.

The prevention of tarnish of metallic restorations may depend upon the addition or variation of certain alloying elements. Precious metals such as palladium and platinum have been noted as being valuable factors for increasing the tarnish resistance of gold alloys to sulphur (6). Crawford (7) showed this effect by adding various amounts of palladium and platinum to gold alloys which were immersed in sulphurized oil and ammonium-sulfide vapor. His results showed that gold alloys containing about 68 to 72 per cent gold and 6 to 8 per cent palladium and/or platinum demonstrated the best resistance against tarnish.

The mechanism of tarnish protection due to palladium and platinum additions has not been clarified. Also, the exact relationship between the amounts of alloying elements such as silver, copper, palladium, platinum, and other elements, and the tarnish resistance of gold base alloys has yet to be clarified. This work is an attempt to elucidate the tarnishing reaction of gold dental alloys with and without palladium in sulfide solutions utilizing electrochemical techniques and microanalysis of surface films following the exposure.

Nature of the Oral Environment

The oral environment is very conducive to the formation of corrosion products. The mouth is moist and continually subjected to fluctuations in temperatures and wide ranges of pH caused by liquids and the breakdown of foodstuffs. Human saliva contains the necessary elements for a good electrolyte, therefore a corrosion cell may exist in the oral cavity between two or more electrochemically dissimilar metals or on a single metallic restoration. The possible path of an electric current in the mouth may exist by passage through tooth structure and saliva. Thus, a knowledge of the oral environment is helpful in understanding the nature of galvanic currents in the mouth.

Teeth are calcified structures set in the alveolar bone of the lower and upper jaws. A tooth is composed of four different tissues: (1) enamel, a hard, brittle substance which covers the exposed portion of the tooth; (2) dentin, a bonelike substance which forms the body of the tooth; (3) pulp, a viscous substance containing blood vessels and lymph which is located in the central cavity of the tooth called the pulp chamber; and (4) cementum, which is a bonelike substance covering the root of the tooth (8).

Saliva is secreted into the mouth by salivary glands, and serves to lubricate ingested food and to begin the breakdown of starches. The composition of saliva will vary from person to person depending upon the genetic constitution of the individual and by his physical and emotional status. Saliva will also have different compositions for a single individual during different periods of the day. Table 1 (9) shows a typical composition of human saliva.

Table 1. Composition of Human Saliva

Inorganic Components		Organic Components	
	mg/100 ml		mg/100 ml
Ca	5.7	Protein	230
P	15.7	Carbohydrate	15
Mg	.4	Cholesterol	25
Na	67.3	Urea	4.5
K	71.0	Uric acid	2.5
CO_2	34.0	Citrate	1.0
Cl	91.4	Lactate	3.0
NH_3	6.5	Creatinine	1.0
Thiocyanate	13.0	Sialic acid	5.0
Fluoride	0.1	Glucose	1.0

The salivary composition may be affected by the source of saliva, flow rate, duration of stimulation, nature of the stimulus, and diet.

Saliva is produced by three major glands: the parotid, the submandibular, and the sublingual. The major ions found in human saliva are phosphate, chloride, bicarbonate, potassium, calcium, and sodium. Only general quantitative differences of these ions in saliva from the salivary gland secretions has been shown. For instance, parotid saliva is high in phosphate and low in calcium when compared to sublingual and submandibular secretions (10). Also, the types of proteins and their concentrations are different in each of the glandular secretions. Saliva also contains a number of nonsalivary components such as leukocytes, gingival fluid, and food debris (11).

The salivary composition is definitely influenced by the flow rate. Generally, when the flow rate is slightly increased above the unstimulated rate, calcium, phosphate, chloride, potassium, and protein concentrations decrease, whereas pH and bicarbonate and sodium concentrations increase. At higher flow rates, bicarbonate, chloride, calcium, sodium, and protein concentrations and pH increase, whereas the potassium concentration shows little change and the phosphate concentration decreases (12-14). The flow rate may be changed due to dehydration and hyperhydration conditions. Hyperhydration has been shown to increase the flow rate, whereas dehydration causes a decrease in flow rate (15, 16).

The composition of the saliva will vary with the duration of stimulation. The calcium, protein, and bicarbonate concentrations and pH will increase whereas the chloride concentration decreases in proportion to the rise in bicarbonate concentration with increased duration of

stimulation. This change in concentration and pH generally occurs within the first one or two minutes of stimulation. This situation of changing concentration and pH may not find a steady state even after fifteen minutes of stimulation (13, 14).

The nature of the stimulus will have a profound effect upon the protein concentration in the parotid and submandibular secretions. It has also been shown that the salivary secretions respond differently to pharmacologic, electric, and taste stimuli (17-19).

Foods that require vigorous mastication will cause an increase in salivary flow rate. Also, foods which are highly flavored tend to increase the salivary flow rate. The increased flow rate will not only change the composition but it will also increase the buffering capacity of the saliva. Saliva has a unique buffering capacity that maintains a fairly constant pH range of 6.3 to 6.8 despite the introduction into the mouth of substances containing high concentrations of acids or alkalies (20, 21).

The metals will be affected by these oral environmental conditions and as a result the magnitude of the corrosion current may vary. Increased corrosion can cause unwanted deterioration, release metallic ions, and may occasionally produce sensitivity.

Alloys for Dental Restorations

Metals present in the oral environment, such as metallic restorations, will undergo reactions with nonmetallic elements to produce chemical compounds. The products of these reactions may be esthically unacceptable and sometimes even physiologically harmful. Therefore, materials must be used which are fairly resistant to the specific conditions of the oral

environment, including fluctuations in temperature and pH.

The alloy most commonly used to satisfy these conditions is dental amalgam which is composed mainly of mercury, tin, silver, and copper. The poor mechanical properties, except compressive strength, of amalgam limits its dental use to fillings.

Cobalt-chromium alloys, containing nickel, molydenum, and minor amounts of other elements, have been used for large dental appliances, primarily partial dentures. They exhibit good corrosion resistance and mechanical properties. Production difficulties such as casting integrity and especially cleaning are the main disadvantages of these alloys.

Gold is another metal with properties that make it suitable for dental use, either pure or in an alloyed form. Pure gold has been used in the form of gold foil for direct fillings. While the pure gold is relatively soft, its hardness increases when it is compacted in the dental cavity. Pure gold exhibits excellent corrosion and tarnish resistance. For use in dental applications requiring higher strength and hardness, gold is alloyed with other elements, primarily copper and silver. Copper, which is an effective strengthener, is used in amounts not exceeding 16 per cent since it has a tendency to give the alloy a reddish color. Silver neutralizes the reddening effect of copper addition and is used in amounts up to 18 per cent. The addition of platinum to gold alloys increases their hardness and resistance to tarnish. Most gold alloys have no more than about 3 to 4 per cent platinum, since platinum has a tendency to whiten the alloy. Palladium may be added since it is an effective strengthener, hardener, and age hardening element. Palladium is often used in place of platinum since it is cheaper. Most dental alloys contain no

more than 3 to 4 per cent palladium since it also tends to whiten the alloy. Figures 1, 2, 3 and 4 show the phase diagrams for copper-gold, palladium-gold, silver-gold, and platinum-gold systems, respectively. Certain other elements such as zinc and nickel have also been added to improve the properties of gold alloys. Zinc is used as a scavenger element since it will combine with any oxides present, while nickel is used as a strengthener.

Gold alloys are used for inlays, crowns, bridge abutments, and removable appliances. There are four major classes of gold alloys which are available for use in the mouth: type I, type II, type III and type IV. Type I and type II are used for inlays in restorations not subject to great stress. Type III is used for crowns, bridge abutments, and inlays where higher stress is applied during mastication. Type IV is employed for removable appliances which require polishing outside of the mouth. Gold alloy wires and solders have also been developed for dental applications. Gold alloy wires are used for construction of clasps for orthodontic appliances and for partial dentures. Gold alloy solders are used principally to build up certain gold structures and to join parts of dental bridge assemblies (6).

Principles of Corrosion

Corrosion is not just the formation of a surface deposit but an actual deterioration of a metal by reaction with its environment. This deterioration of a metal may occur through the action of moisture, atmosphere, alkaline or acid solutions, and certain chemicals. The oral environment and dental structures present conditions that can promote corrosion and discoloration.

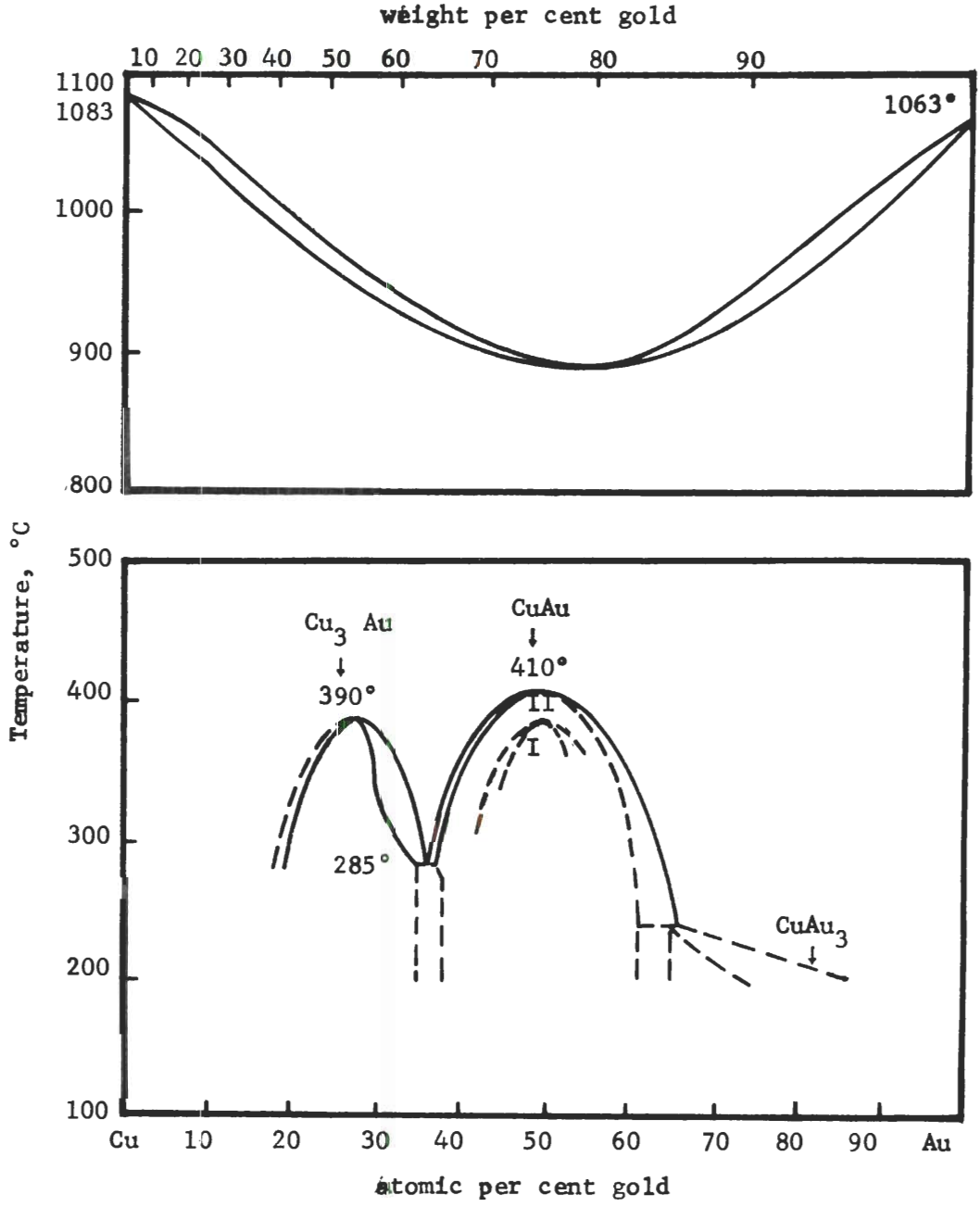

Figure 1. Copper-Gold Phase Diagram.

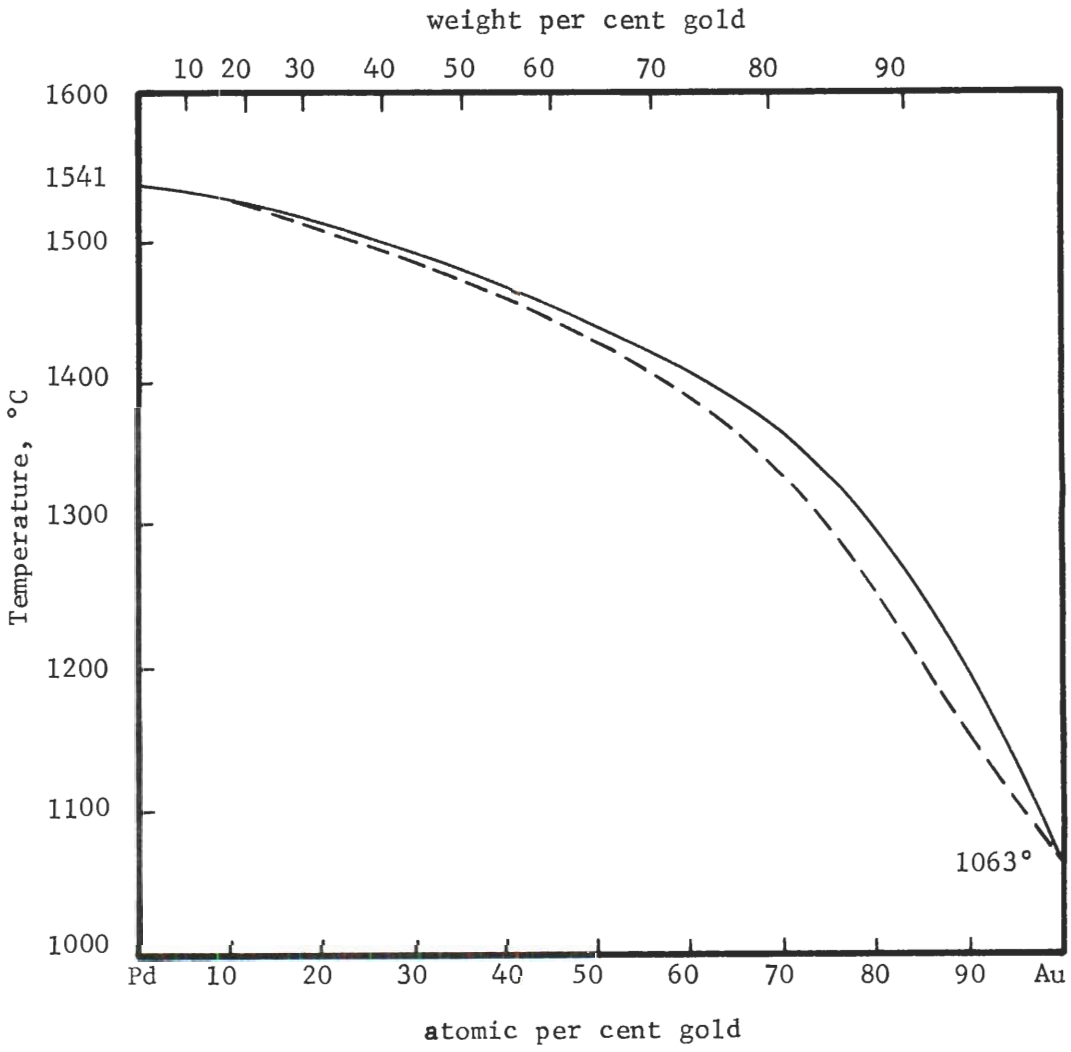

Figure 2. Palladium-Gold Phase Diagram.

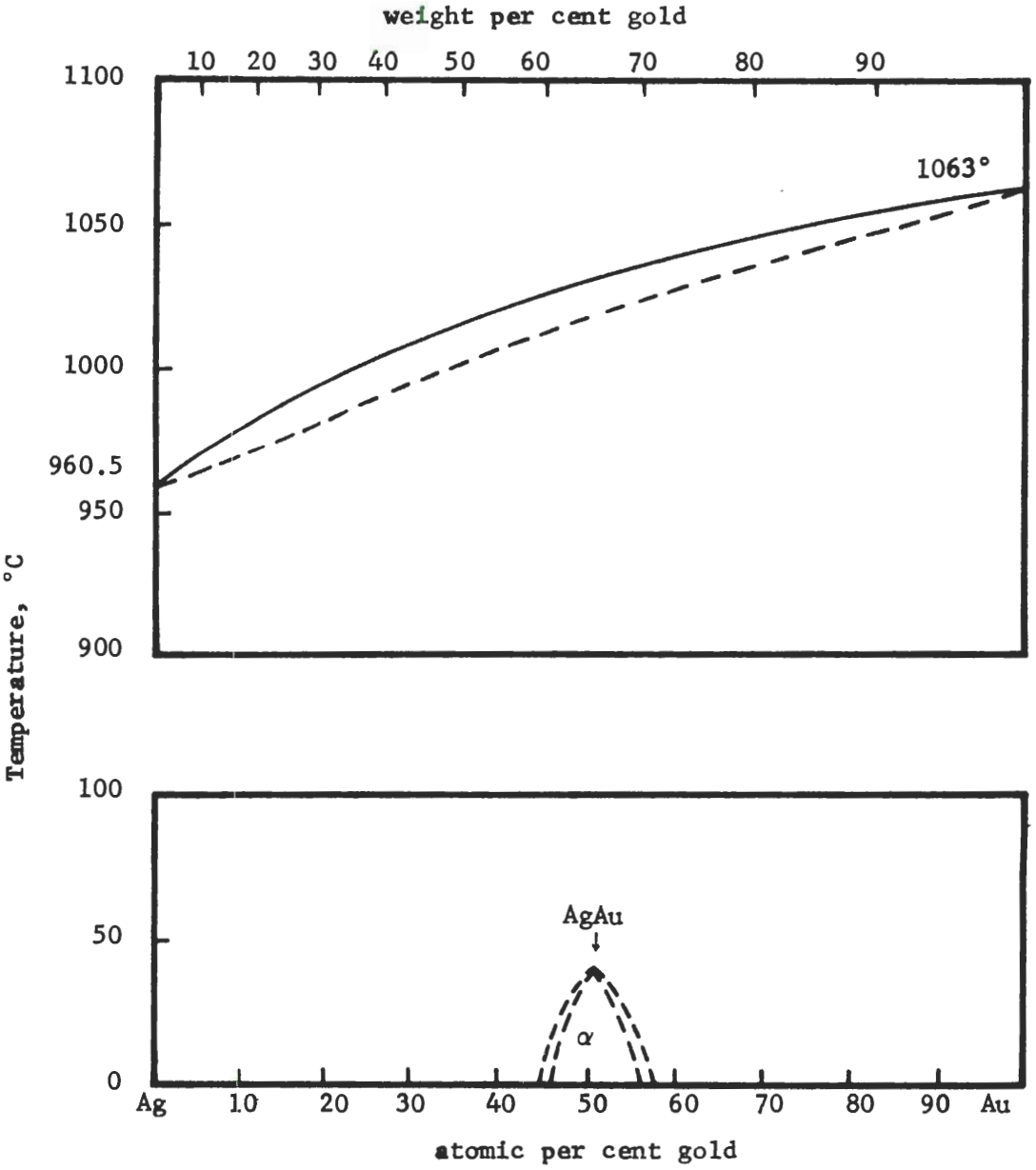

Figure 3, Silver-Gold Phase Diagram.

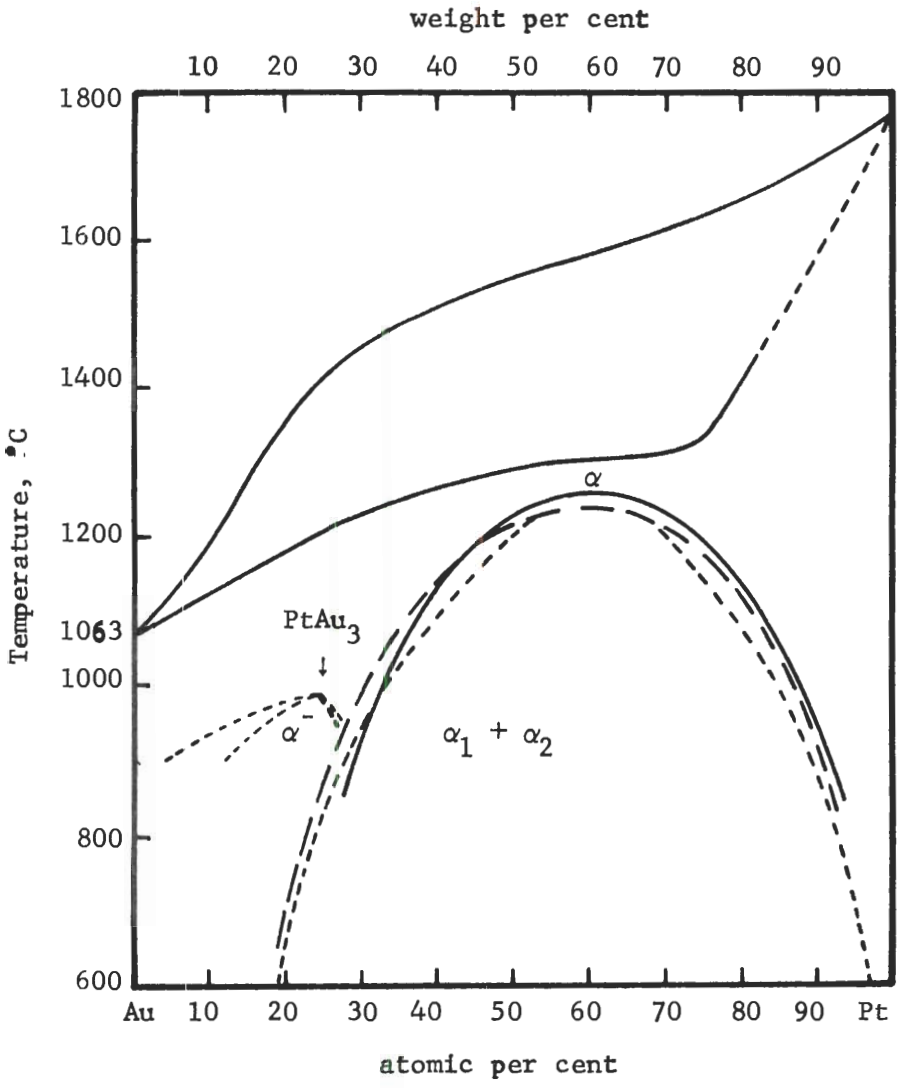

Figure 4. Gold-Platinum Phase Diagram.

Electrochemical corrosion occurs in aqueous conditions such as the oral environment. The phenomenon of electrochemical corrosion is characterized by a flow of electrical current through an electrolytic cell which may be the result of two dissimilar metals in contact or due to differences on a metallic surface resulting in anodic and cathodic sites. The anodic site is characterized by metallic ions going into solution according to the oxidation reaction

$$\text{Metal} \rightarrow \text{Metal}^{z+} + Z \text{ electrons} \quad (23).$$

On the cathodic sites, electrons are consumed in a reduction process. This reduction process may involve the liberation of hydrogen gas on the metallic surface according to the reaction

$$2H^{+} + 2 \text{ electrons} \rightarrow H_2,$$

or the reduction of dissolved oxygen,

$$O_2 + 2H_2O + 4e^{-} = 4OH^{-},$$

or other cathodic reactions.

The current for electrochemical corrosion results from the difference in the electorde potentials. In Table 2 (24), some common electrode reactions are arranged in the order of their equilibrium potentials under standard conditions, with respect to the hydrogen electrode. The potential under non-standard conditions will depend upon the concentration of metallic ions in the solution according to the Nernst equation:

$$E_{Metal} = E_o + \frac{RT}{zF} \ln a_{Me^{z+}}$$

Table 2. Standard Electrode Potentials

Electrode Reaction	Potential (volts, SCE)
$Au \rightleftarrows Au^{+} + e^{-}$	+1.691
$Au \rightleftarrows Au^{3+} + 3e^{-}$	+1.498
$2H_2O \rightleftarrows O_2 + 4H^{+} + 4e^{-}$	+1.229
$Pt \rightleftarrows Pt^{2+} + 2e^{-}$	+1.2
$Pd \rightleftarrows Pd^{2+} + 2e^{-}$	+0.98
$Ag \rightleftarrows Ag^{+} + e^{-}$	+0.799
$Cu \rightleftarrows Cu^{+} + e^{-}$	+0.521
$Cu \rightleftarrows Cu^{2+} + e^{-}$	+0.337
$Cu \rightleftarrows Cu^{2+} + e^{-}$	+0.153
$H_2 \rightleftarrows 2H^{+} + 2e^{-}$	0.000
$Sn \rightleftarrows Sn^{2+} + 2e^{-}$	-0.136
$Mo \rightleftarrows Mo^{3+} + 3e^{-}$	-0.20
$Ni \rightleftarrows Ni^{2+} + 2e^{-}$	-0.250
$Co \rightleftarrows Co^{2+} + 2e^{-}$	-0.277
$Cr \rightleftarrows Cr^{3+} + 3e^{-}$	-0.744

where E_{Metal} is the electrode potential of the metal, E_o is the standard electrode potential of the metal, R is the gas constant, T is the absolute temperature, z is the valency, F is the Faraday constant, and $a_{Me}z+$ is the activity of the metal ions. As the metallic ion concentration in the solution approaches equilibrium, the tendency of the metal to dissolve decreases.

At equilibrium, the rates of the forward and reverse reactions are equal. If the equilibrium is disturbed, so that the electrode potential departs from the reversible value, the electrode is said to be polarized. If the potential changes to a more positive value, the polarization is said to be anodic; the forward (oxidation) reaction is encouraged, and a net (dissolution) current flows. At potentials more negative than the reversible value, the net current will be cathodic. The relation between the current density and the over potential, $\eta = E - E_{reversible}$, is given by the Tafel equation

$$\eta = a \pm b \log i$$

where a and b are constants and i is the density of the current flowing through the electrode (25). When the anodic current is due to the dissolution of the metal, the relation between the current and weight loss, W, is given by the Faraday law:

$$W = \frac{M}{nF} It$$

where I is the galvanic current in amperes, M the atomic weight of the anode metal, n the charge of the metal ions formed, F the Faraday constant, and t the time of flow of current in seconds (26).

The relation between electrode potential and current can be

illustrated in a polarization diagram which is shown in Figure 5 (27). The Tafel equation gives a straight line relationship when the electrode potential is plotted against the logarithm of the current or current density, in the so called Tafel region. At higher current densities, the reaction rate may be limited by the rate of diffusion of the species involved, giving rise to concentration polarization. If the metal forms a protective surface film, the electrode which is anodically polarized will undergo an active-passive transition in a certain potential range (Figure 5). When the potential reaches the primary passivation potential (E_{pp}) during anodic polarization, the current density, which has reached the critical current density for passivation (i_{cp}), drops to a very low value. An increase in current will appear at higher potentials due to oxygen evolution, oxidation to higher valency state, or localized breakdown of the passive film.

In addition to active, passive, and transpassive conditions, a metal electrode can also be in a state of immunity if the potential is below the reversible potential of the dissolution reaction. In the state of immunity, corrosion is thermodynamically impossible. The electrochemical state of a metal depends on the potential and pH of the solution. For pure metals, these relationships are illustrated in potential-pH (Pourbaix) diagrams in which the ranges of thermodynamic stability of possible phases are shown.

The corrosion potential of a metal electrode is a mixed potential which lies between the potentials of the anodic and cathodic reactions. Since the rates of the anodic and cathodic reactions must be equal to preserve electrical neutrality, the corrosion potential is given by the

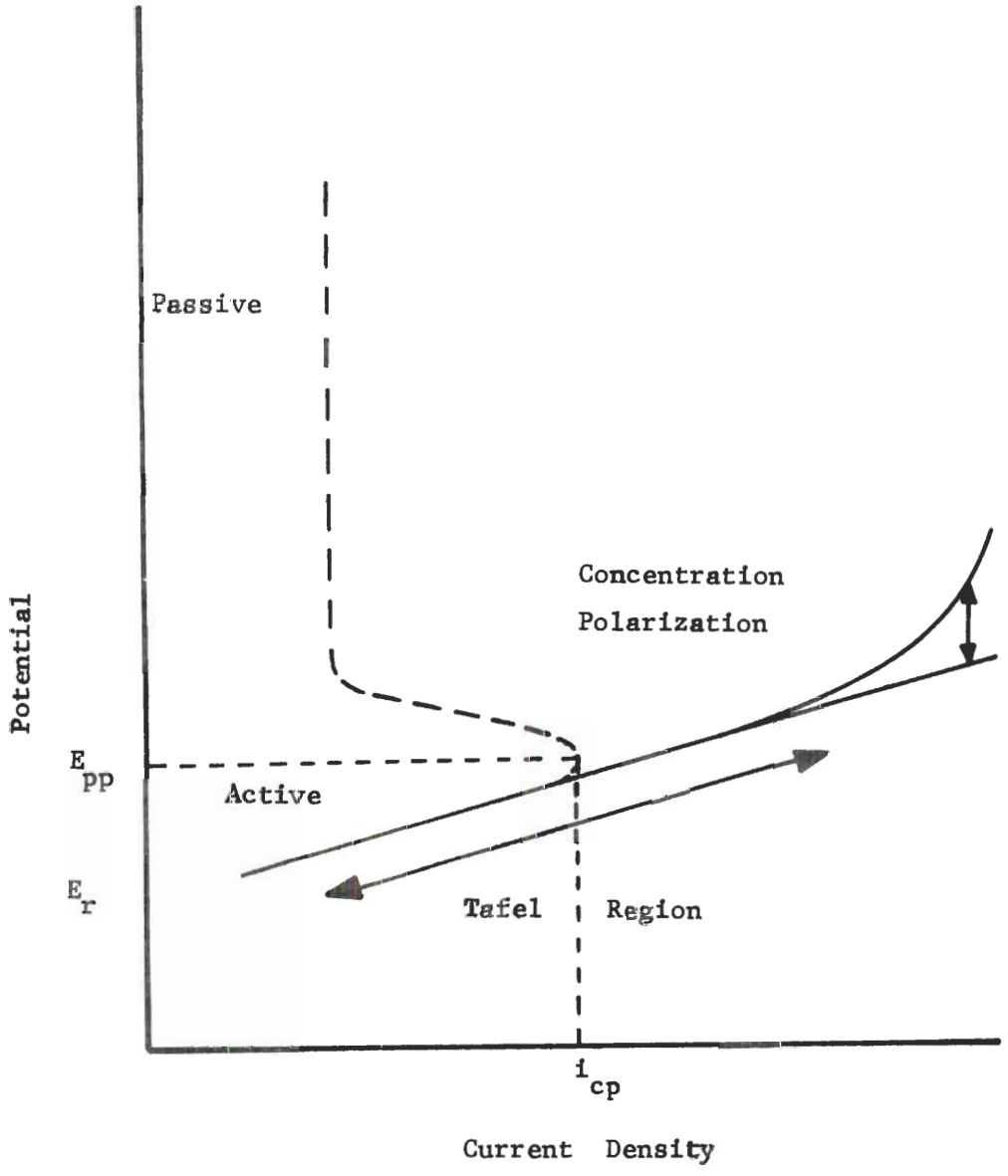

Figure 5. Schematic Polarization Diagram.

intersection of the anodic and cathodic polarization curves, as illustrated in Figure 6 (25).

Corrosion Processes on Metallic Restorations

In the mouth, various conditions may result in electrochemical reactions taking place. If two dissimilar metals are used in such a way that a conductive path exists between them, corrosion current will result from the potential difference of the two metals resulting in a typical galvanic cell. In the mouth, the electrolyte can be the saliva, tissue fluid, soft tissue, and blood depending on the environment the metal contacts. The magnitude of such a galvanic current between a gold and an amalgam restoration in the mouth was reported as approximately 0.5 microamperes (28).

The possibility of currents occurring in the oral environment is not confined to two dissimilar metallic restorations. A cell may also be created on a single restoration due to differences in the composition of the electrolyte. This type of cell is known as a concentration cell. One of the electrolytes may exist at the margin of the restoration due to oxygen depletion and pH changes by the settling of foods or drugs at the margin, or in pits, pores, and other crevices in the restoration in which the mass transport is restricted. The current flow in such a cell is caused by the potential differences between the external surface of the restoration and the surface in the margin, because the single electrode potential depends on the concentration and composition of the electrolyte.

A current may also be produced due to the heterogeneous composition of the metal surface. If two or more phases are present in the structure of an alloy immersed in an electrolyte, there will be potential differences

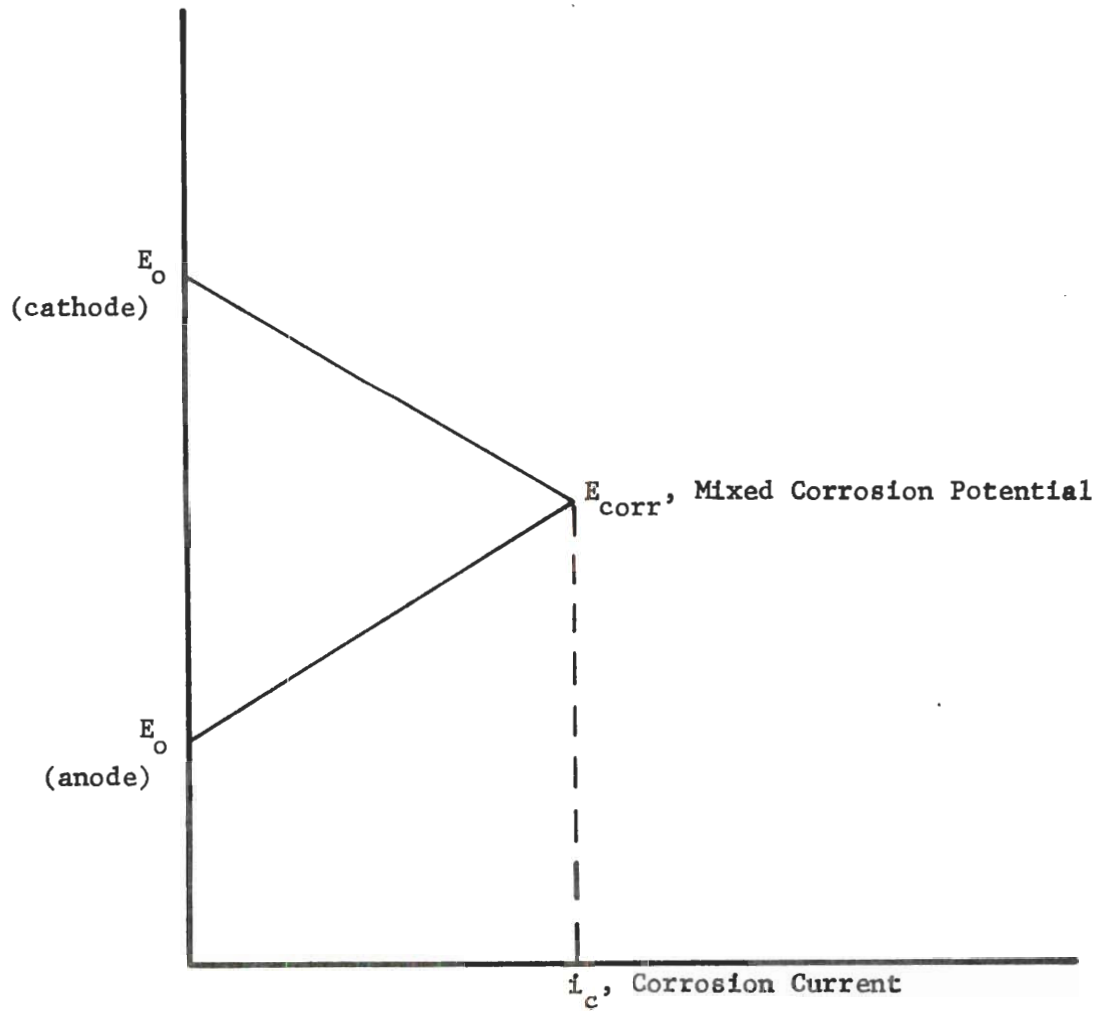

Figure 6. Combined Activation Polarization Curves for an Anodic and Cathodic Reaction on a Corroding Specimen which is Anodically Polarized.

on the surface of the alloy resulting in the flow of local currents. Other inhomogeneities, such as a cored structure, will behave similarly (6).

Auger Spectroscopy

The identity of the elements composing a film on the surface of a metal is of primary significance when corrosion is considered. Auger analysis is an important new technique used for the study of extremely thin films deposited on the surface of the metal. The metal is bombarded by low energy electrons which ionize the inner orbits of some of the atoms at the metal's surface. When one of the atom's electrons drops from a higher energy level to the ionized level, an electron can be ejected from the atom without the emission of electromagnetic radiation. This electron is referred to as an Auger electron. These electrons enter the curved electrostatic-deflection energy analyser which acts as a sorter to keep electrons with too much energy or too little energy from entering the electron multiplier system. An energy distribution curve is obtained by this technique, the peaks being characteristic for the elements present, however, Auger peaks on the curve are small and are superimposed on a relatively large background. As a result, a plot is made of the derivative of energy distribution with respect to energy, that is, a plot of the slope of the distribution curve. The derivative will emphasize the Auger peaks on the smooth background (29).

CHAPTER II

PROCEDURES AND METHODS

Materials

The dental gold alloys were prepared by J. F. Jenlenko and Company. The alloys were prepared in 200 gram melts by induction melting. The metal was then poured into an ingot which was heated at 1300°F for two hours after which time the metal was quenched in water. Upon cooling, the ingot was rolled and cut into small pieces. These small pieces were then melted individually and cast in a centrifugal casting machine and allowed to bench cool. The composition of the alloys are listed in Table 3.

Sample Preparation

Each cast disc sample was cut into approximately equal pieces to be mounted. The mounting consisted of attaching a copper wire approximately 11 cm in length to the specimen by means of a conductive glue. A 7 millimeter glass tubing was then fitted over the copper wire. The glass tubing prevents the copper wire from coming into contact with the aqueous solution. The sample was then placed in a teflon mold which was filled with epoxy. The epoxy was allowed to harden at 70°C. After the epoxy has hardened, the mounted samples were wet-surface ground on 180 through 600 carbide grit abrasive papers and then polished with 0.3 micron aluminum oxide on a rotating velvet cloth. The samples were then dipped in ethyl alcohol and dried under a stream of hot air.

Table 3. Composition of Dental Alloys

Sample	Weight per cent			
	Au	Ag	Cu	Pd
1	72.0%	11.0%	17.0%	0.0%
2	71.0%	16.0%	13.0%	0.0%
3	73.5%	6.5%	20.0%	0.0%
A	72.0%	10.5%	17.0%	0.5%
B	72.0%	10.0%	17.0%	1.0%
C	72.0%	8.0%	17.0%	3.0%
D	72.0%	5.0%	17.0%	6.0%

Potential-Time Measurements

Samples were immersed in 5 per cent sodium sulfide and synthetic saliva solutions to determine corrosion potentials with respect to immersion time. A saturated calomel electrode (SCE) was used as a reference electrode. The potential was read off of an electrometric digital multimeter every 30 minutes. The synthetic saliva was prepared from reagent grade chemicals according to the formula given by Tani and Zucci (30) since this particular formula very closely resembles natural saliva. Carbon dioxide (CO_2) was bubbled into the synthetic saliva in order to maintain a constant pH of about 6.8. A stirrer was used to keep the saliva agitated. The pH was monitored by means of a Leeds and Northrup pH meter.

Auger Spectroscopy

The samples used for Auger spectroscopy were mounted in lucite and polished by a procedure already described. The samples were immersed in 5 per cent Na_2S solution for a period of two weeks at the end of which time they were removed from the solution and washed with distilled water and dried under a stream of hot air. Samples 1, A, and B were removed from lucite mountings and were mounted in a molydenum sample holder. They were then placed in an ultra-high vacuum system capable of less than 5×10^{-9} torr without subsequent heating of the sample or the Auger system. The system is shown schematically in Figure 7. Two electron guns were used to provide electrons for bombardment of the samples. One gun was normal to the surface of the specimens and the other gun was angled to graze the surface of the samples. The two guns are used to give relative compositional differences depending on the thickness of the surface film.

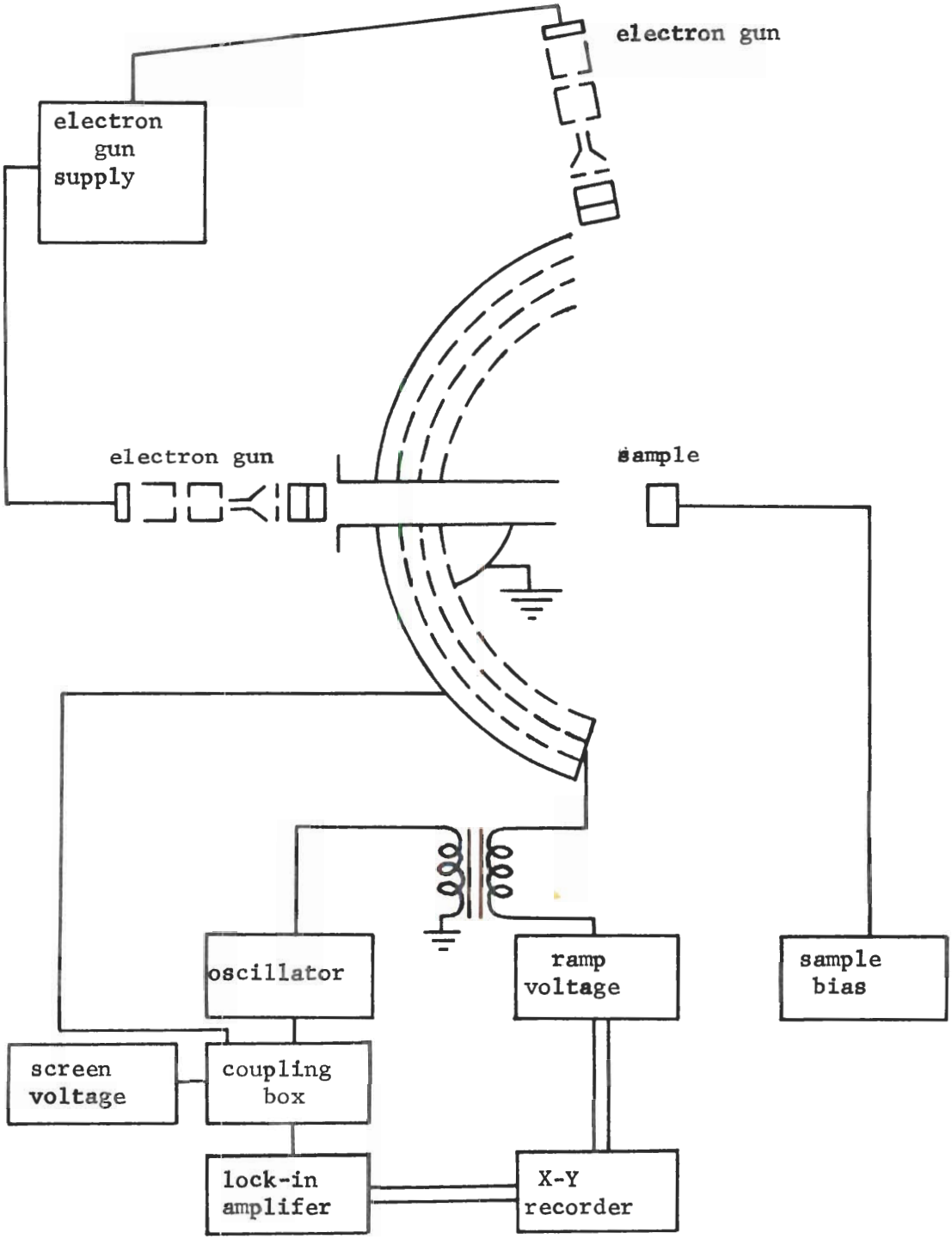

Figure 7. System for Auger Analysis.

Polarization Measurements

A Wenking model 68TS3 potentiostat was used for the determination of anodic polarization curves. The reference electrode was a saturated calomel electrode, while the auxillary electrode was platinum. The electrodes were immersed in 5 per cent sodium sulfide (pH 12.5) and Beckman buffer (pH 12.45) solutions. The solutions were deaerated for one hour before potentiostatic measurements began. The potential was increased in a stepwise fashion at a rate of 6 mV/min (in steps of 2 mV). The current and potential were recorded on an X-Y recorder. The samples were polarized anodically over a range from -1.2 to +.8 volts (SCE). Sample 2 was scanned at three different potential rates in sodium sulfide solution. The potential rates were .6 mV/min, 6mV/min, and 60 mV/min. The current and potential were again recorded on an X-Y recorder.

Knoop Hardness Measurements

The gold alloys were mounted in lucite and were wet-surface ground up to 600 grit emery paper and polished with 1.0 and 0.3 micron aluminum oxide. The mounted samples were washed with ethyl alcohol and dried under a stream of hot air. A Wilson Tukon hardness tester was used for the measurements of Knoop hardness. A total of fifteen different readings were made on each sample under a load of 100 grams.

CHAPTER III

DISCUSSION OF RESULTS

Potential Versus Time Measurements

The open circuit potentials as measured in a 5 per cent Na_2S solution are presented in Table 4 for all samples. The open circuit potentials were measured at the end of a 24 hours period since no appreciable change was observed after this period. The open circuit potentials for all gold alloys were very close having a potential range varying from -0.68 to -0.74 volts (SCE). The additions of palladium seems to cause little, if any, effect at all in changing the open circuit potentials of the gold alloys.

The open circuit potentials were also measured in synthetic saliva as shown in Figure 8. It is noted that samples 1 and 2 showed potentials of -0.077 and -0.045 volts (SCE), respectively, after eight hours. The samples containing palladium and sample 3 showed more noble potentials ranging from +0.12 to +0.18 volts (SCE). Sample 3 contained the highest copper content and least silver content of the non-palladium gold alloys. It is observed that the addition of only 0.5 per cent palladium to sample 1 gives a more noble potential than those of the samples without palladium.

Auger Analysis

The samples used for Auger analysis were visually observed for surface film formation after the exposure to sodium sulfide for two weeks. It was noted by visual examination that sample 1 showed more

Table 4. Open Circuit Potentials of Gold Alloys in 5 per cent Na_2S Solution.

Gold Alloy Samples	Potential Relative to SCE (volts)
1	-.69
2	-.72
3	-.70
A	-.71
B	-.71
C	-.69
D	-.74

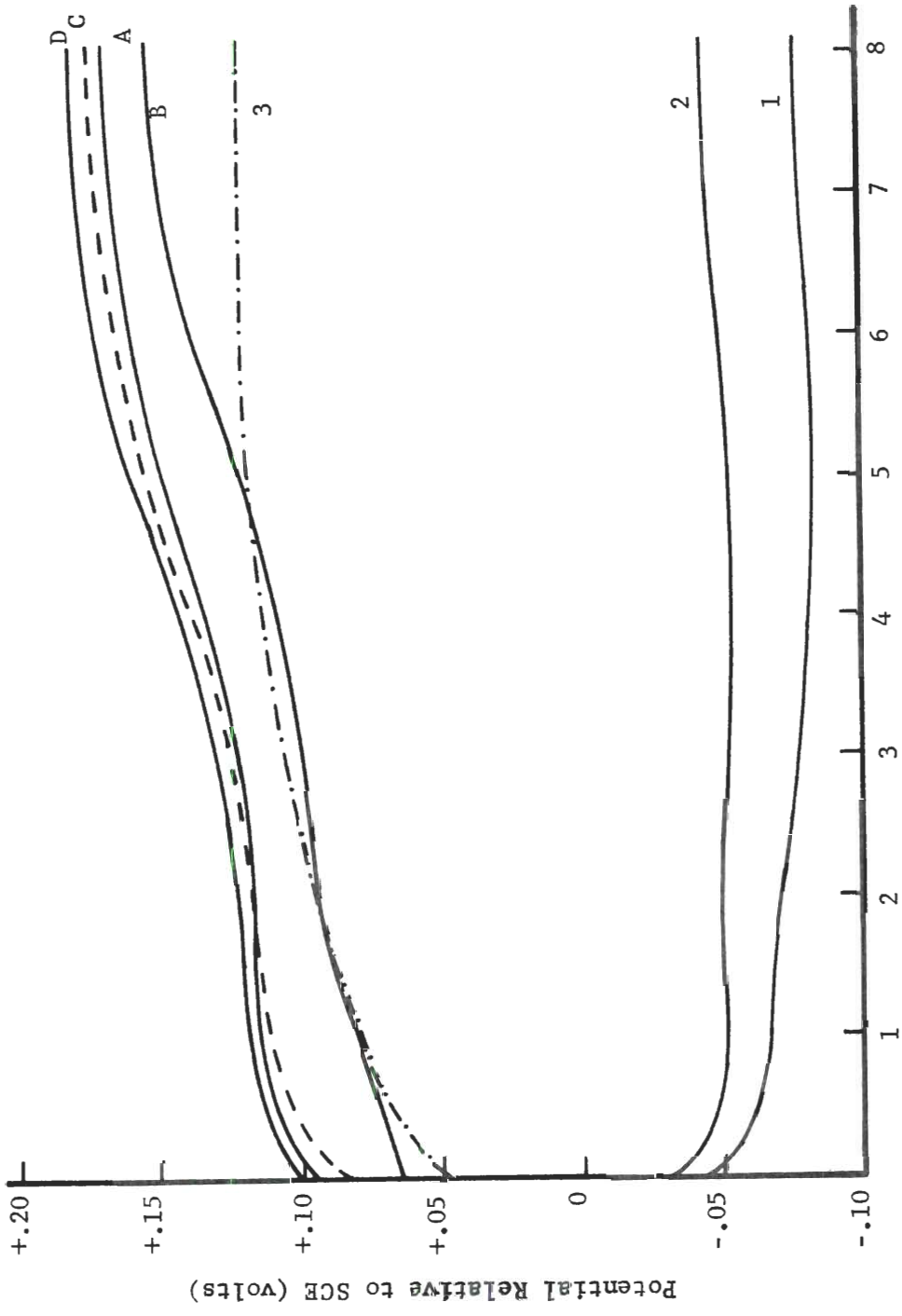

Figure 8. Potential Versus Time Curves for Gold Alloys in Synthetic Saliva.

surface of the sample and appeared as a bluish-black substance. Figure 9 shows the results from the surface film of sample 1 using the grazing gun. The surface film consists of sulfur, chlorine, silver, oxygen, and sodium. Figure 10 gives the results using the normal incidence gun on sample 1. The film is composed of sulfur, carbon, silver, and sodium. Figures 11 and 12 show the film compositions on samples A and B, respectively, using the grazing electron gun. The compositions are sulfur, carbon, silver, chlorine, oxygen, and sodium. Figures 13 and 14 show the composition of surface films as detected by the normal incidence electron gun for samples A and B. The surface film of sample A is basically composed of sulfur, carbon, silver, sodium, oxygen, and chlorine. Sample B gave similar results as sample A. The carbon is present due to alcohols which were used to clean the samples before the exposure. Sodium and chlorine are probably surface contaminates due to the handling of the samples. The oxygen is present due to exposure to the atmosphere. The major constituent of the surface film formed on the gold alloys immersed in 5 per cent Na_2S solution appears to be silver sulfide (Ag_2S).

The maximum depth of penetration for the electrons was about 5 to 6 atomic layers or 30 Å. The Auger analysis was not able to detect any immediate layers which may lie between the maximum depth of penetration and the surface of the metal. It is possible that a sublayer of a copper compound could exist in the surface film below 30 Å.

Polarization Measurements

Anodic polarization curves at three different polarization rates in 5 per cent sodium sulfide solution were obtained for sample 2 as shown in Figure 15. The peak current density increased with the polarization

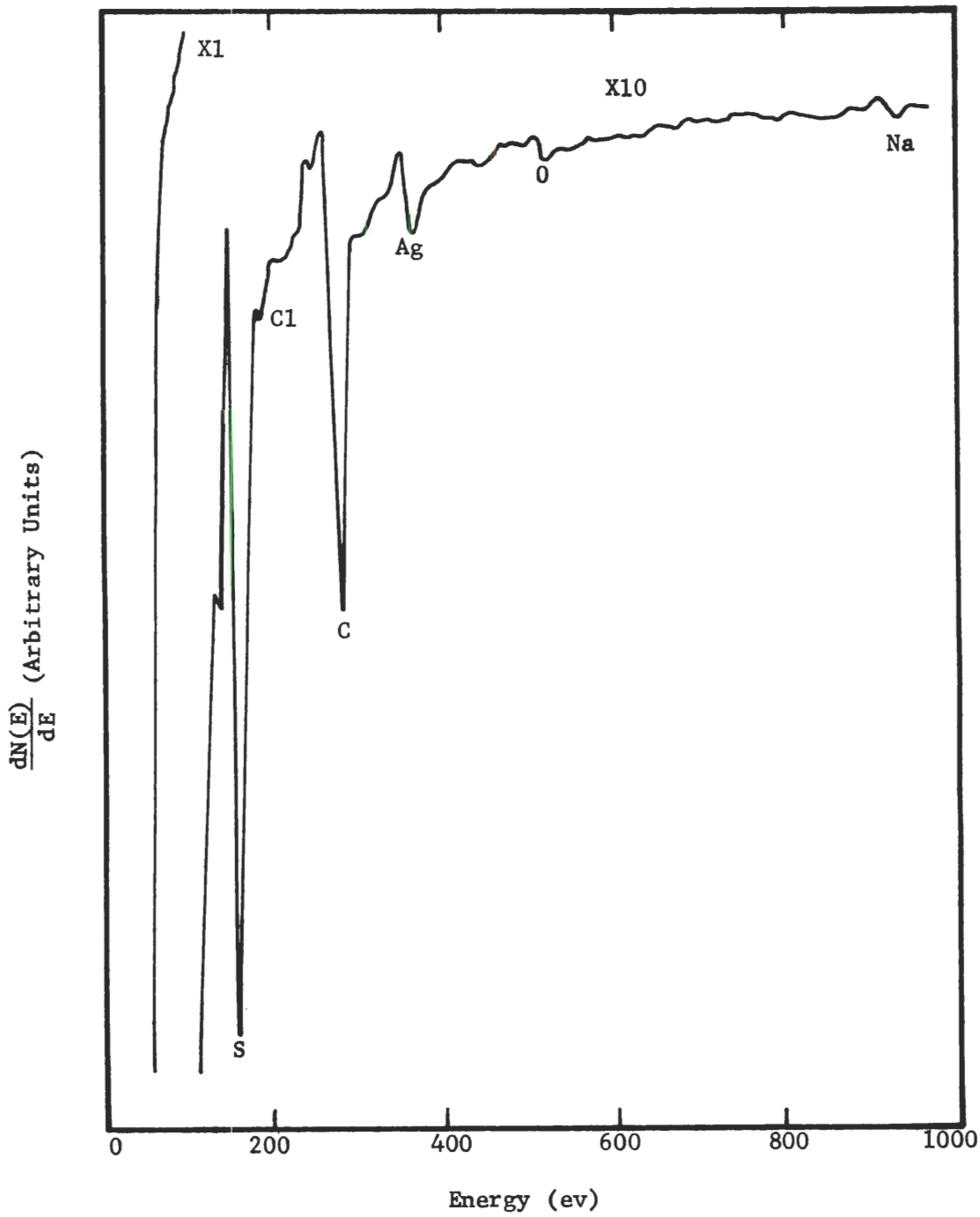

Figure 9. Auger Spectrum for Sample 1 with Grazing Gun.

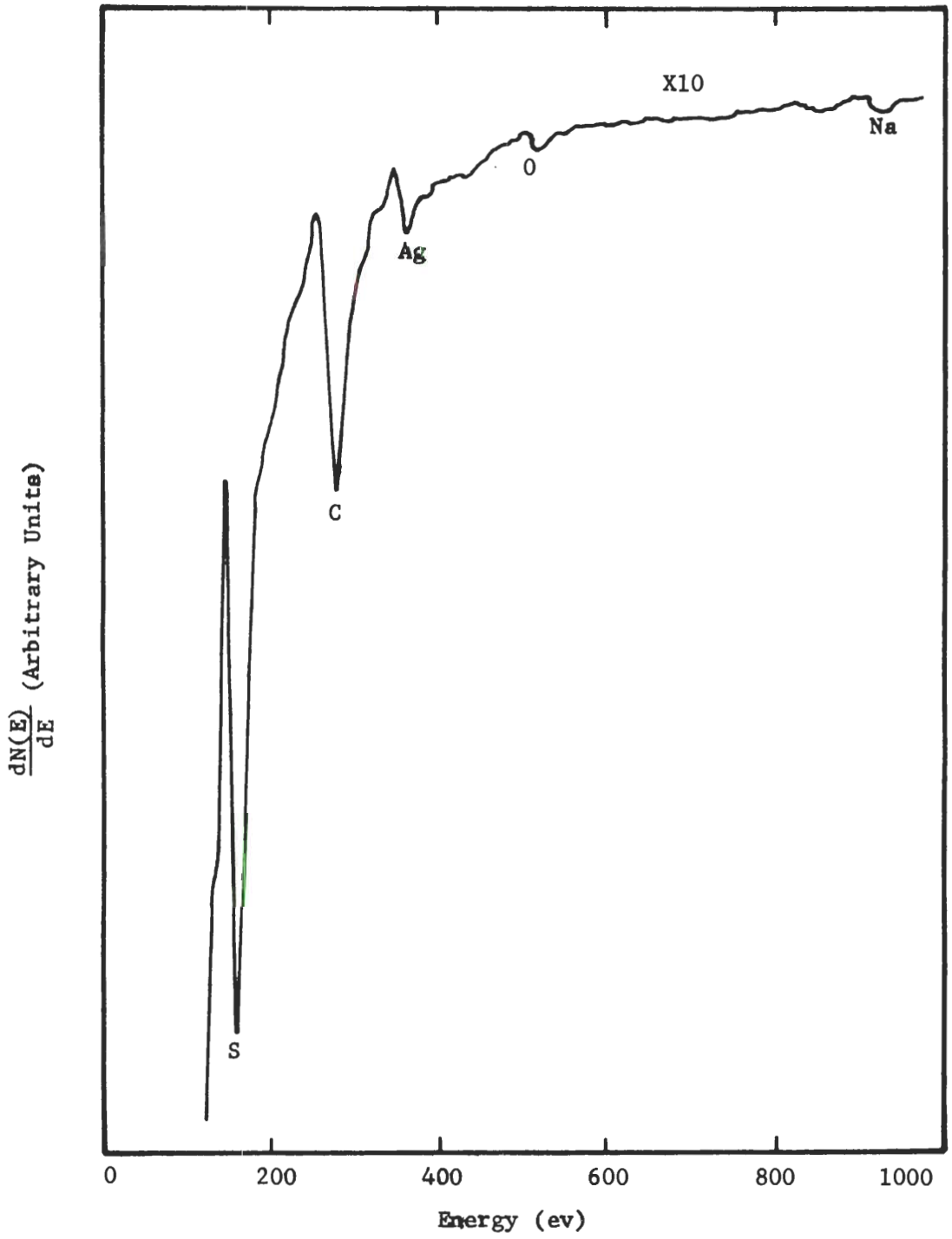

Figure 10. Auger Spectrum from Sample 1 with Normal Gun.

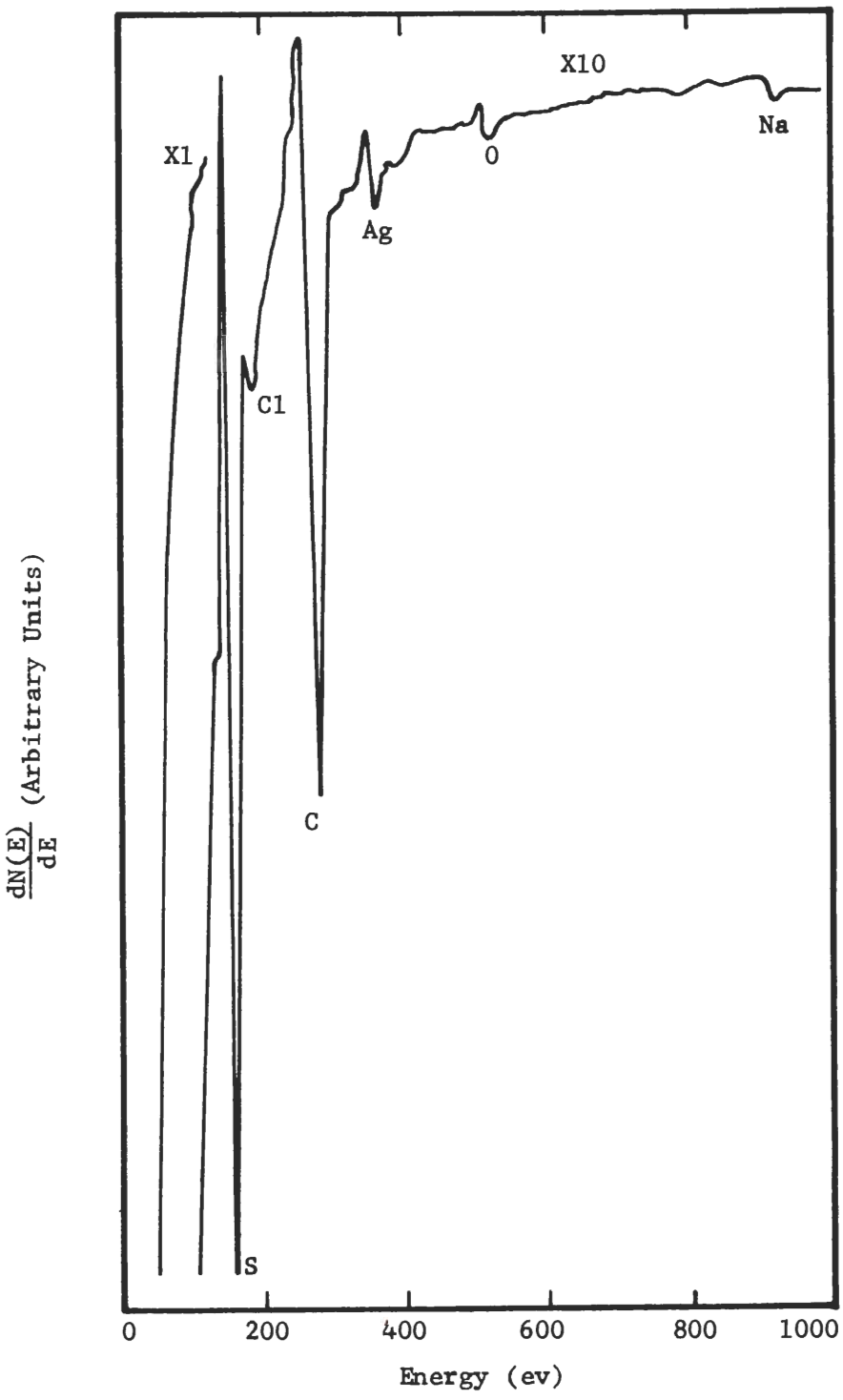

Figure 11. Auger Spectrum from Sample A with Grazing Gun.

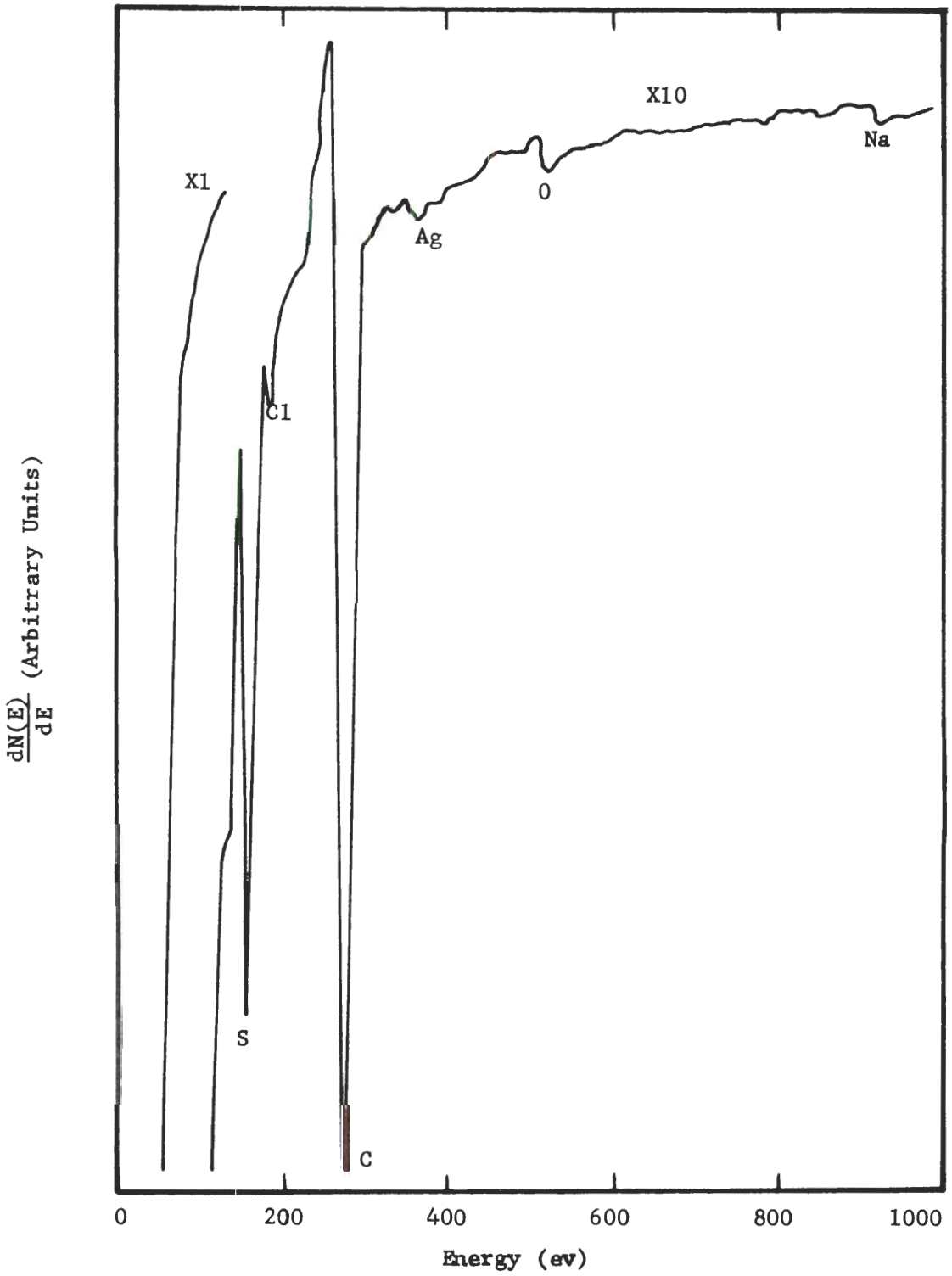

Figure 12. Auger Spectrum from Sample B with Grazing Gun.

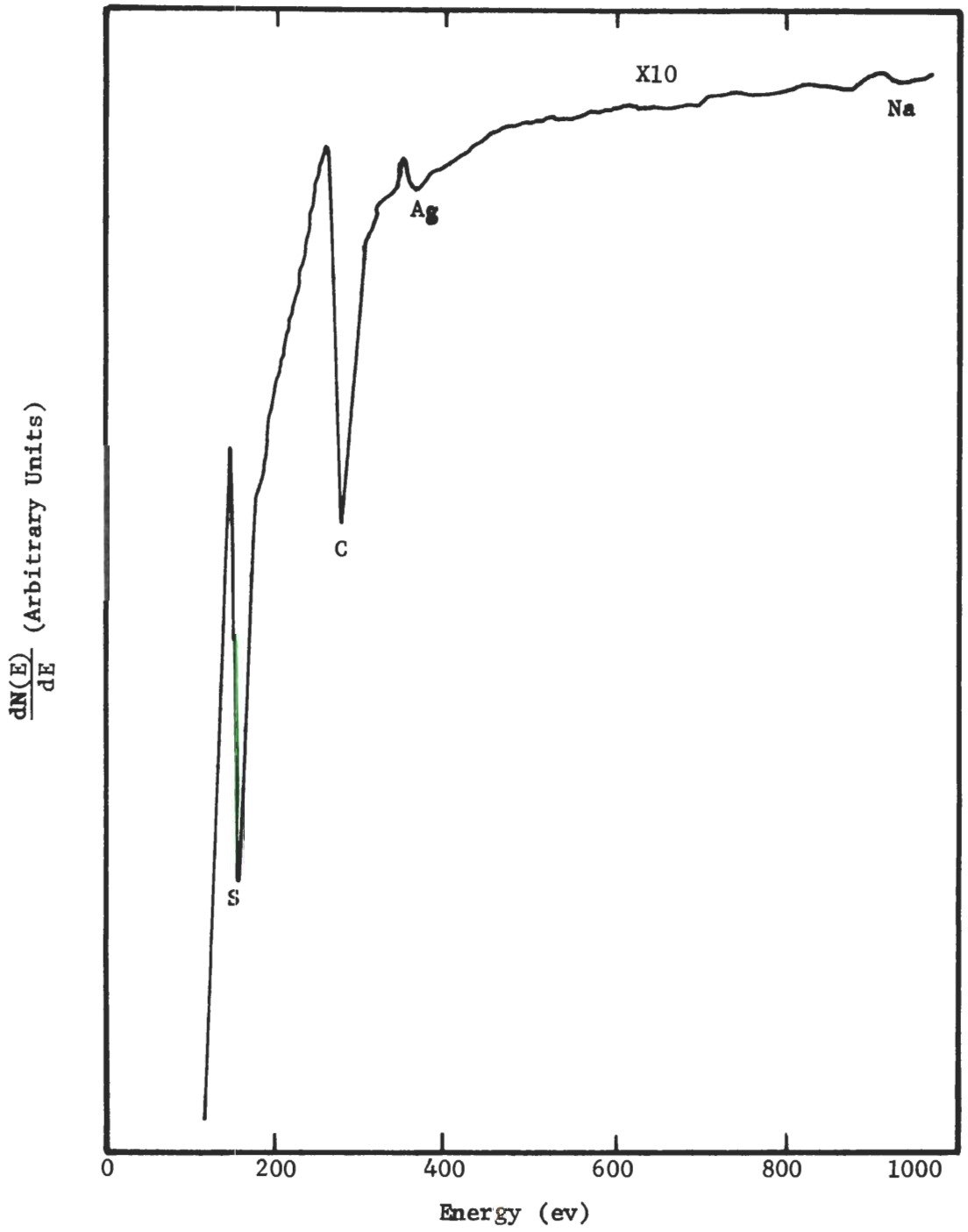

Figure 13. Auger Spectrum from Sample A with Normal Gun.

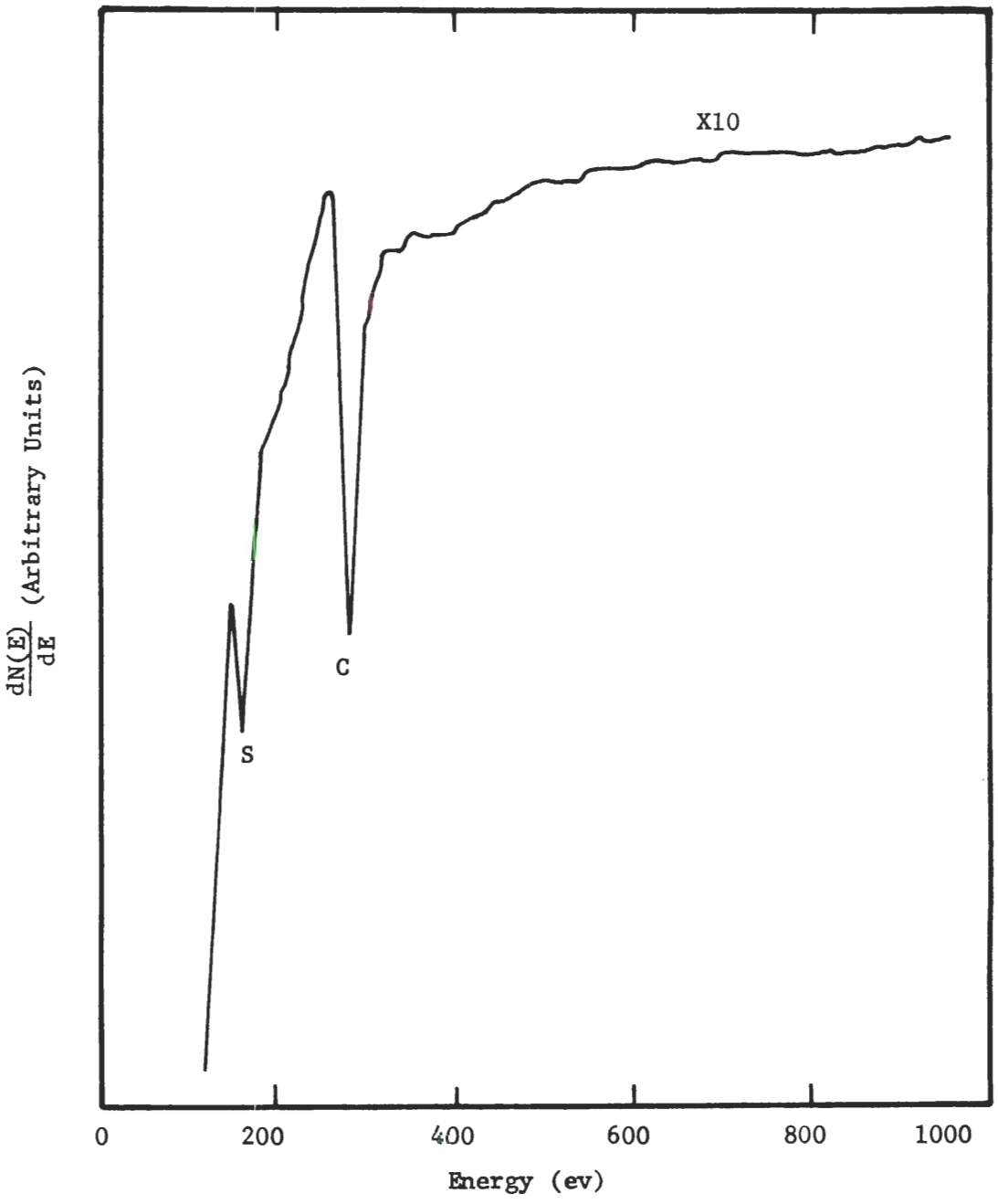

Figure 14. Auger Spectrum from Sample B with Normal Gun.

rate and the potentials of the peaks shifted to more noble values with increased scanning rate. At a high polarization rate (60 mV/min), the second curve overlaps the third curve.

At very low polarization rates, the system is closer to equilibrium at which the onset of a peak would correspond to the equilibrium potential of the reaction in question. With increasing scanning rate, some overpotential is observed and the potentials are shifted in the direction of scanning. The increase in current density is due both to the non-steady state condition and to the fact that to form a certain limiting thickness of a surface film the total amount of electricity needed is constant; the current thus can be lower if the time of formation is increased.

Figure 15 shows that the three peaks on the polarization curves are developed most clearly at a polarization rate of 6 mV/min. Therefore, this rate was used in the rest of the polarization measurements.

The effects of varying the alloy composition on the potentiostatic polarization curves of dental gold alloys in 5 per cent sodium sulfide solution are shown in Figure 16. All three samples show three relatively similar peaks. The samples showed a primary peak at about -0.61 volts (SCE) and secondary and tertiary peaks at -0.48 and -0.37 volts (SCE). It is observed that the primary, secondary, and tertiary peaks of samples 2 and 3 occur at much lower current density values than those of sample 1. The peaks may represent the reactions for the formation of compounds such as Ag_2S, CuS, and Cu_2O. According to Latimer (23), the equilibrium potentials for formation of these compounds are -0.934, -0.784, and -0.602 volts (SCE), respectively.

It is quite possible that the curve from sample 1 gives different

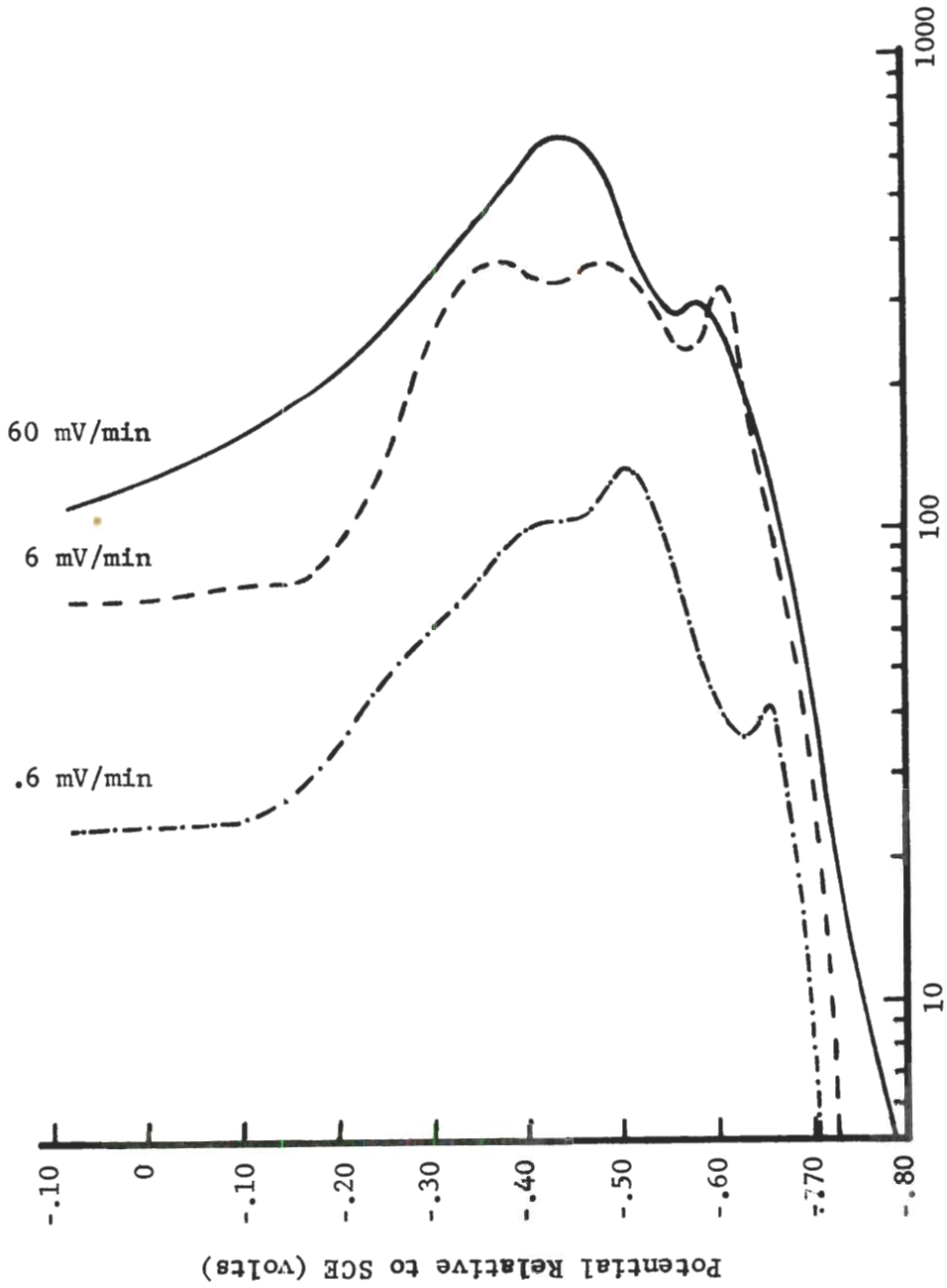

Figure 15. Anodic Polarization Curves for Sample 2 at Three Different Scanning Rates.

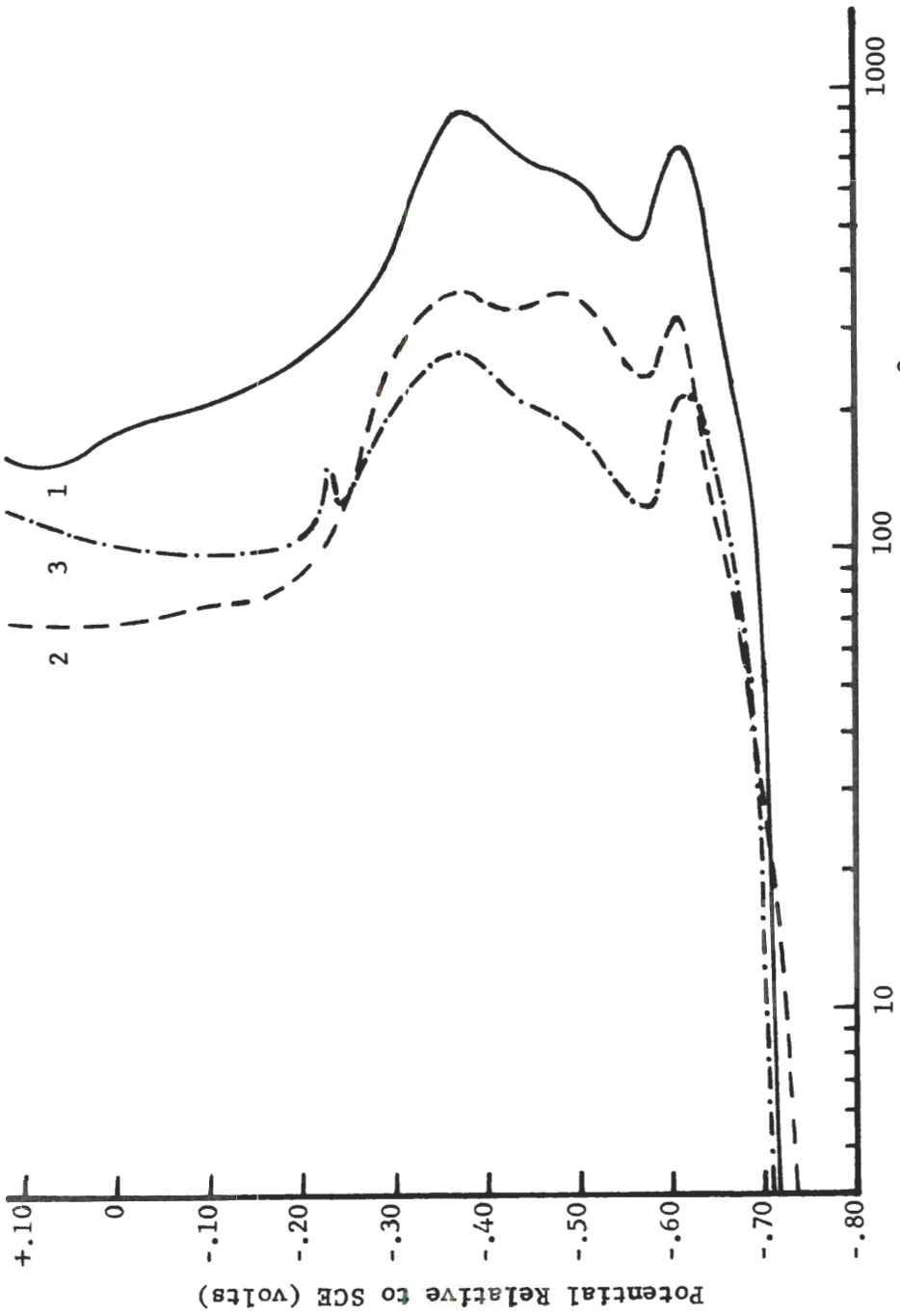

Figure 16. Anodic Polarization Curves for Samples 1, 2 and 3.

values of current density due to other factors. Sample 1 has a gold and silver content which is between samples 2 and 3 but its curve may actually lie between the curves of those two samples; the high currents measured on sample 1 may be due to the unusually high amount of porosity present on the surface of the alloy which increases the effective surface area of the electrode. All of the gold alloys had some porosity present which may have affected their polarization curves to some extent. Figure 17 shows the porosity which is present on the surface of sample 1. Samples 2 and 3 showed a general porosity less than sample 1. The gold alloys containing palladium showed some porosity which may be classified as pinhole and gas inclusion porosities. These pinhole and gas inclusion porosities are due to the entrapment of gases during solidification. It is known that molten palladium has a high affinity for hydrogen as well as for oxygen (4). It is evidenced from the surface structure of the gold alloys containing palladium that gases such as hydrogen or oxygen may have been trapped in the molten state and released upon solidification. The gold alloys containing palladium showed increased porosities with increasing amounts of palladium. Samples B and D are shown in Figures 18 and 19 which show the effects on surface porosity caused by the addition of 1 per cent and 6 per cent palladium.

The additions of various amounts of palladium in place of silver affects potentiostatic polarization curves as shown in Figure 20. The polarization curve for sample 1 has also been plotted for comparison. Samples A and B show two peaks; the first occurring at -0.62 volts (SCE) for both samples. The second peak occurs at -0.42 volts for sample A and -0.36 volts (SCE) for sample B. Samples C and D show a primary peak as

Figure 17. Optical Micrograph of Sample 1 (50X).

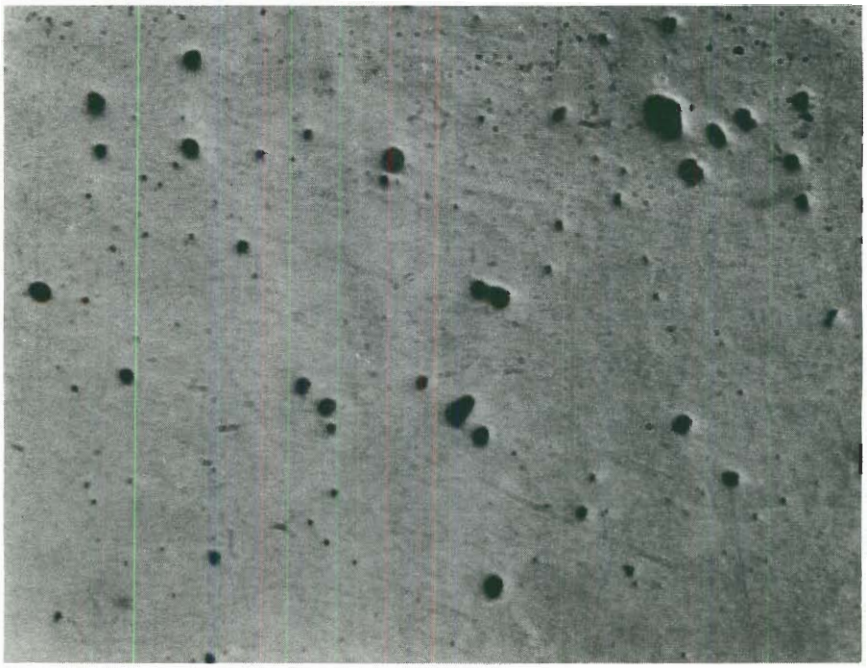

Figure 18. Optical Micrograph of Sample B (50X).

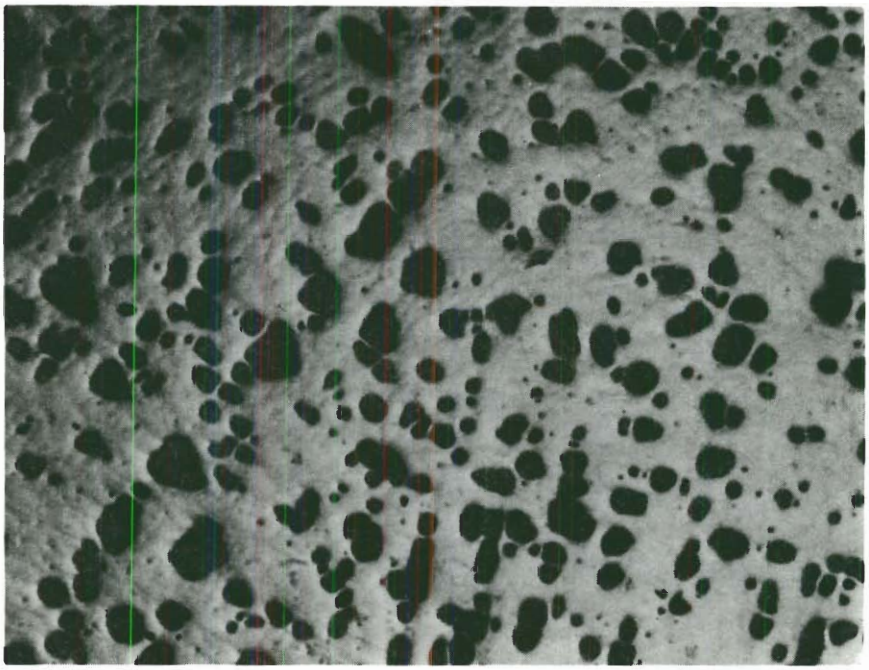

Figure 19. Optical Micrograph of Sample D (50X).

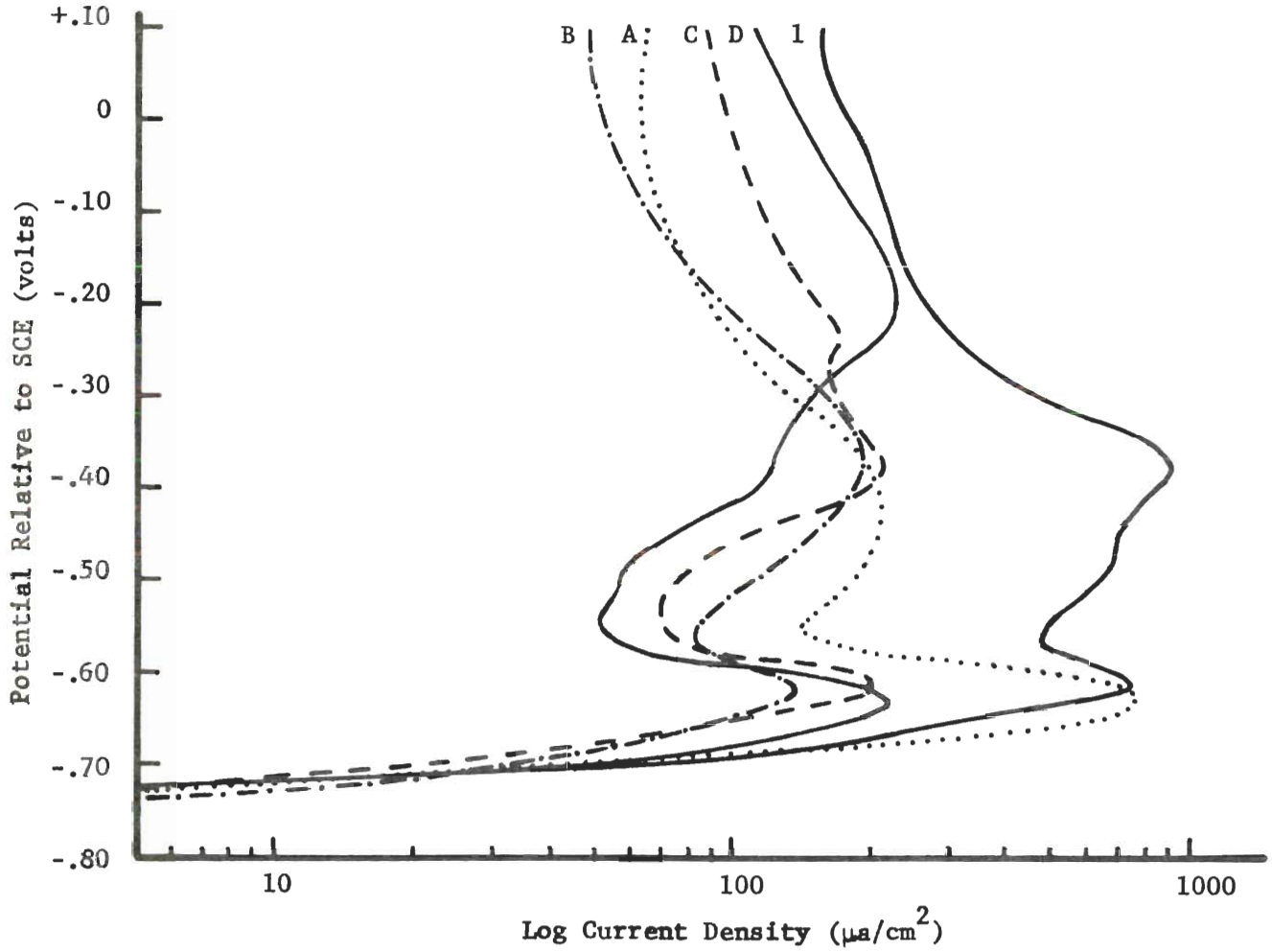

Figure 20. Anodic Polarization Curves for Samples 1, A, B, C and D.

well as secondary and tertiary peaks. Primary peaks for samples C and D are at -0.61 and -0.63 volts (SCE), respectively. Sample C has two peaks occurring at -0.38 volts and at -0.19 volts (SCE). The addition of palladium tends not only to reduce the current density in each of the four samples, but it also tends to shift the secondary and tertiary peaks to higher potentials. The addition of palladium did not add any new peaks to the polarization curves for gold alloys containing palladium. It is safe to assume that no palladium compounds will form as surface films on the samples in the potential range used.

The three peaks in Figure 20 may again represent the reactions of formation for Ag_2S, CuS, and Cu_2O. A fourth peak not shown on Figure 20 was also observed for samples A, B, and D occurring at the potential of -1.06 volts (SCE). The polarization curves for samples 1, 2, 3, and C did not show this peak. This peak was probably obscured by the high hydrogen evolution taking place at such low potentials. It is quite possible that this peak may represent the reaction for the formation of Cu_2S. Latimer (23) gives the potential of formation for Cu_2S to be -1.174 volts (SCE). The potentials given by Latimer are the potentials at which the compound first begins to form, not at which the reaction takes place at a maximum rate. The peaks on the polarization curves represent maximum reaction rates.

The potentiostatic polarization curves of samples 1 and C in a buffer solution of pH 12.45 are shown in Figure 21. Both samples have distinct and similar peaks. Sample 1 shows two peaks at potentials of -0.39 and -0.08 volts (SCE). Sample C also has two peaks occurring at -0.44 and -0.18 volts (SCE). The peaks may represent the reaction of

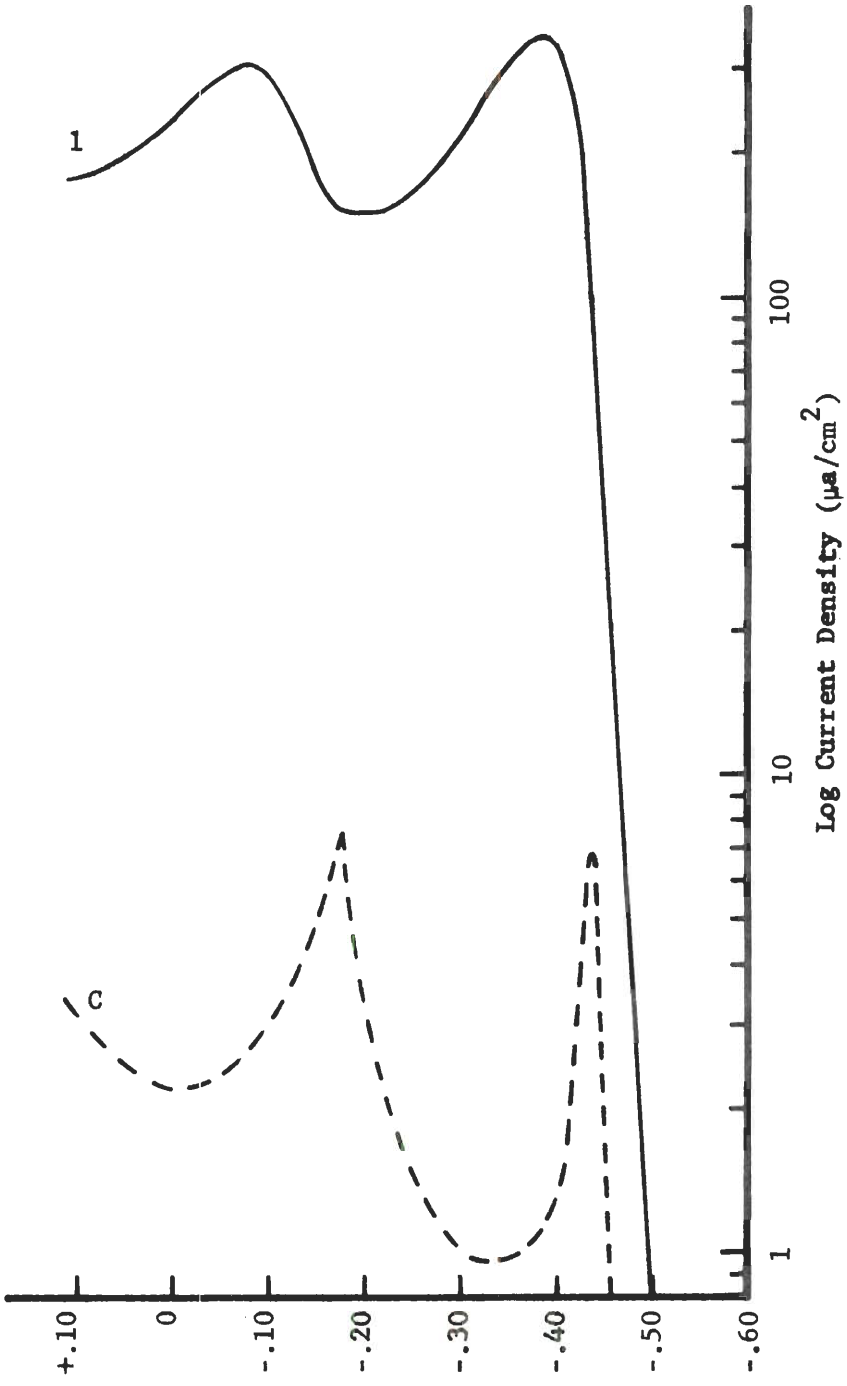

Figure 21. Anodic Polarization Curves for Samples 1 and C in Buffer Solution.

formation of copper compounds such as Cu_2O and CuO. According to Pourbaix diagrams (31), the equilibrium potentials for formation of these compounds are -0.523 and -0.324 volts (SCE) at this pH. A comparison of polarization curves from Figures 20 and 21 verifies that Cu_2O is represented by the peak at the potential of -0.38 volts (SCE) on Figure 20.

Knoop Hardness Measurements

The results of Knoop hardness testing are shown in Table 5. The gold alloys containing palladium showed hardness values varying from 227 to 305. The gold alloys without palladium showed hardness values higher than samples A, B, and C. This difference in hardness may be a result of a possible difference in heat treatment and grain refinement between samples 1, 2, 3, and A, B, C, D, or a fundamental difference in the order-disorder reaction characteristics due to the palladium addition. The readings may have been affected by the porosity which was present to some extent in all samples. Because of this only the highest readings were used for each sample, since these readings would best represent the true hardness of the samples.

Discussion of Possible Effects of Palladium Additions on Tarnishing

The element palladium is a transitional metal lying in group VIII of the periodic chart. Palladium is one of the transitional metals which contains a full d-shell of electrons. According to Engel (30), the more d-electrons which are present the greater will be the bonding strength between two metals when alloyed. Palladium added to the gold alloys will accordingly form very strong bonds with the constituent metals making up the gold alloys. By increasing the bonding strength, this in turn will

Table 5. Knoop Hardness Numbers

Sample	Hardness Numbers
1	292
2	285
3	350
A	227
B	245
C	263
D	305

increase the activation energy of the constituent metals, such as silver, in the reaction with the environment. Thus, this increased bonding strength as a result of the addition of palladium seems to increase the difficulty for silver to take part in the formation of the compound silver sulfide. This is a possible explanation since it was shown that the palladium did not cause any significant changes in the open circuit potentials of the gold alloys. It appears that the palladium may also change the physical metallurgy of the alloy, i.e., the order-disorder transformation, which may affect the tarnish resistance.

CHAPTER IV

CONCLUSIONS

1. The major constituent of the tarnish film observed on the surface of the gold alloys immersed in sodium sulfide solution was identified as silver sulfide.

2. The reaction for the formation of Cu_2O occurring on the surface of gold alloys in deaerated buffer solutions was verified by polarization curves. It was also observed from polarization curves that the reactions for the formation of CuS and Cu_2S may also occur in the oral environment on gold restorations but these compounds were not identified in the tarnish film.

3. The addition of palladium to gold alloys decreases the susceptibility of the alloys to tarnishing. This may be due to an increase of the activation energy for the reaction of silver with sulfur as a result of increased bonding strength between palladium and silver atoms in the alloy.

4. The gold alloys with and without palladium showed casting porosity. The porosity seemed to increase the susceptibility of the alloys to tarnishing.

CHAPTER V

RECOMMENDATIONS

1. The effect of the addition of palladium on the physical metallurgy of gold alloys should be investigated by techniques such as x-ray diffraction, mechanical testing, electrical conductivity measurement, etc.

2. The effects of changes in physical metallurgy on the electrochemical behavior of these alloys should be investigated.

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